10-009-399

#2

T/AU00/00366

AUSTRALIA

AU 00/00366

4

Patent Office
Canberra

REC'D 16 MAY 2000
WIPO PCT

I, LEANNE MYNOTT, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PP9893 for a patent by VINPAC INTERNATIONAL PTY LTD filed on 22 April 1999.

COMMONWEALTH OF AUSTRALIA
AUSTRALIA
PATENT OFFICE

WITNESS my hand this
Eleventh day of May 2000

LEANNE MYNOTT
TEAM LEADER EXAMINATION
SUPPORT AND SALES

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

VINPAC INTERNATIONAL PTY LTD

ORIGINAL

AUSTRALIA
PATENTS ACT 1990

PROVISIONAL SPECIFICATION FOR THE INVENTION ENTITLED:

"TREATED CLOSURES 2"

This invention is described in the following statement:

BACKGROUND TO THE INVENTION

This invention relates to improved closures for use in connection with food or beverages. One application is in relation to improved closures for wine bottles.

Wine bottles have traditionally been stoppered with corks made from natural cork material. However, this material can be subject to initial flaws, or deteriorate in use, resulting in contamination or spoilage of the wine. For example, oxidation of the wine, due to permeation of oxygen through the cork into the wine, results in vinegar flavour. "Cork taint", due to the presence of trichloro-anisoles (TCA) and other flavour active compounds in the cork, imparts a musty or mouldy smell and flavour to the wine. Leakage can also be a problem. Furthermore, cork is a relatively expensive material, as most supplies still come from Portugal.

None of the alternatives to natural corks proposed to date have been entirely satisfactory.

Plastic stoppers and screw-cap stoppers may be as effective as natural corks, but have not yet been tested adequately over the prolonged storage periods of quality red wines. Furthermore, there is considerable consumer resistance to use of such stoppers, particularly for quality wines.

Accordingly, there have been numerous attempts to improve on natural cork stoppers, by coating or impregnating them.

The first cork coatings were simply lubricants such as paraffin and Vaseline. These merely ensured that the cork was easier to insert into the bottle and later remove, without disintegration. The other problems associated with cork stoppers were not addressed. Furthermore, the compounds used as lubricants generally tend to melt under conditions necessary for pasteurisation (50-100° C).

Currently, materials used in surface treatment of corks include oils and silicone resins, emulsions of various formulations, as well as some plastic coatings. These coatings do prevent leakage of the wine, but do not provide a barrier against taint and oxidation.

Many of these coatings also present problems with the coating coming off the cork and leaving an oily layer on the wine surface.

Hybrid corks have been moulded from natural cork and synthetic cork cells made from a plastic polymer. The synthetic cells fill the gaps between the cork cells, and a binding agent (such as polyurethane) is used to bind the cells together. However, hybrid corks have to date proved unsatisfactory, as they often leak and can disintegrate and be difficult to extract from a bottle.

The present invention provides an improved closure having a surface coating or diffusion layer comprising an appropriate polymer. This coating or diffusion layer has many properties which are of benefit when used (for example) in relation to corks for wine bottles. The coating or diffusion layer limits oxygen permeability, inhibits or prevents the diffusion of trichloro-anisoles (TCA) and other flavour active compounds

into the wine, adheres strongly to the cork and/or penetrates into the surface of the cork, is sufficiently flexible to be capable of withstanding compression and decompression during the corking process, enables the coated cork to be readily extracted from the bottle, reduces or prevents wine leakage, is resistant to sulphur dioxide, has long life under ethanolic conditions, and is acceptable to the food and beverage industry with respect to toxicology (ie it is non-toxic or does not leach into the wine).

These coatings or diffusion layers are also applicable to substrates other than cork (eg packaging and wrapping materials) which are directly or indirectly in contact with food products or beverages.

SUMMARY OF THE INVENTION

According to the present invention, an appropriate polymer, having functional groups which are reactive with a substrate and with one or more flavour active compounds (eg TCA), is applied as a surface coating or diffusion layer to said substrate, said substrate being for use in direct or indirect contact with food products or beverages. The substrate may, for example, be a bottle closure (such as a cork), packaging and wrapping materials (such as packaging for cheese), or a bottle or other container.

As mentioned above, the polymer is selected so as to be reactive with both the substrate and with at least one flavour active compound (eg TCA). Accordingly, the polymer may comprise functional groups which contain covalent bonds with polarity, which allow interaction with the polar flavour active compounds or the substrate. For example, the

hydroxyl group is polar, with electropositive groups being attracted to the electronegative oxygen atom, and electronegative groups being attracted to the electropositive hydrogen atom. Alternatively, hydrogen bonds can serve as a bridge between two electronegative atoms, holding one by a covalent bond and the other by pure electrostatic forces.

As already mentioned, the polymer has functional groups which are reactive with a substrate and with one or more flavour active compounds. Accordingly, the polymer coating or diffusion layer, in addition to acting as a partial physical barrier to the passage of gases (eg oxygen) and flavour active compounds, also forms a chemical barrier to the passage of flavour active compounds. The polymer is also selected to be sufficiently flexible for its proposed use (eg to withstand compression and decompression during the corking process, if the substrate is a cork), and be acceptable to the food and beverage industry with respect to toxicology (ie it is non-toxic or does not leach into the food product or beverage). Furthermore, if the substrate is a cork, the polymer coating or diffusion layer must enable the coated cork to be readily extracted from the bottle, prevent wine leakage, and have long life under ethanolic conditions. Preferably, the polymer coating or diffusion layer will also be resistant to sulphur dioxide and changes in pH.

DETAILED DESCRIPTION OF THE INVENTION

Suitable polymers and copolymers which may be used include those described in the following references:

J.Wen, G. L. Wilkes, Polymer Bulletin,1996, 37, 51-57

J. Hazziza-Laskar, G. Helary, G. Sauvet, J. Appl. Polym. Sci., 1995, 58, 77-84

Tezuka et. al., Macromolecules, 1995, 28(24), 8251-8258

P. Schofield, C. Cohen, C. K. Ober, Polymer Gels & Networks, 1998, 6(3-4), 291-300

T. Furuzuno, K. Seki, A. Kishida, T. Ohshige, K. Waki, I. Maruyama, M. Akashi, J. Appli. Polym. Sci.,1996, 59, 1059-1065

D. Spridon, L. Panaitescu, D. Ursu, C. V. Uglea, I. Popa, R. M. Ottenbrite, Polymer International, 1997, 43, 175-181

J. C. Schmidhauser, K. L. Longley, J. Appli. Polym. Sci., 1990, 39, 2083-2096

L. Lestel, H. Cheradame, S. Boileau, Polymer, 1990, 31, 1154-1158

G. E. Hahn, K. D. Klein, I. Yilgor, C. Could; In Silicone-Containing Polymers Editor, R.G. Jones; The Royal Society of Chemistry: Cambridge, UK; 1995; pp 81-87

M. A. Sherman, J. P. Kennedy, J. Appli. Polym. Sci., 1998, 30, 1891-1899

Examples are:

polyurethanes and copolymers and ionomers

terephthalate copolymers

polyethylene vinyl alcohol

(vinylidene) copolymers

epoxies and copolymers

polyamides and amide copolymers

styrene-acrylonitrile (SAN)/acrylonitrile-butadiene-styrene (ABS) copolymers

poly (methacrylic acid) and copolymers

poly (methyl) methacrylate and copolymers

Bisphenol copolymers

Bisphenol A (BPA) - epichlorohydrin

cellulose derivatives and copolymers

polyacetal

polyvinylacetate (PVA) copolymers

functionalised silanes (eg comprising amino or thiol groups)

siloxane copolymers, eg comprising polyethylene glycol (PEG), isoprene, butadiene, lactone, amino, terephthalate, amino acid, heterocyclic, hydride (SiH) or epoxy functionalities

Polyethylene vinyl alcohol, functionalised silanes and functionalised siloxanes (eg amino-, epoxy- or hydride-substituted siloxanes) have been found to be particularly suitable.

Modifications of the polymers may be necessary to improve resistance to reactions with various components of the food product or beverage (eg wine).

The method of applying the polymer to the substrate will be dependent on the nature of the polymer and of the substrate, and will include such conventional processes as film formation, adsorption from solution, reactive-adhesion to cork, melt polymer application (eg thermoforming, vacuum forming and plasma polymerisation), UV curing and Corona discharge processes. The polymers may also be components of multilayer laminate structures.

Preferably, the substrate (eg cork) is prewashed with a solution (eg ethanol, water or a mixture of ethanol and water) and then dried before coating, to remove any surface contamination.

The following examples form an overview of some of the technologies which may be used. These examples are illustrative, but not restrictive, of the present invention.

SYNTHESIS OF COPOLYMERS

EXAMPLES:

Hydrosilylation of Polybutadiene

A mixture of polybutadiene (M_n = 400, 9.1g, 0.023mol), triethoxysilane (4.2g, 25mmol), H_2PtCl_6 (0.8ml) in toluene, was refluxed for 24 hours under nitrogen at 110°C. The solution was then allowed to cool, and solvent and excess triethoxysilane was evaporated under vacuum to give a pale yellow oil as a product. The product was confirmed by ^1H nmr.

Hydrosilylation of Polyisoprene

The reduction of Ni(acetylacetonate) (78mg, 0.3mmol) in polyisoprene (M_n = 800,000, 12.0g, 0.015mmol) with $AlEt_3$ (0.6mmol in 0.6 mol hexane) was carried out anaerobically, using an ice bath for cooling. After addition of triethoxysilane (4.2g, 25mmol), the mixture was set aside at room temperature. The reaction mixture was then evaporated to remove excess triethoxysilane and solvent to give the product, which was confirmed by ^1H nmr.

Hydrosilylation of Polyethylene Glycol Methyl Ether

A mixture of the polyethylene glycol methyl ether (5.5g, 16mmol), allyl bromide (3.5g, 29mmol), sodium hydroxide pellets (1.2g, 30mmol) and n-hexane (6ml) was refluxed at 66°C for 17 hours and was allowed to cool. Solvent and the non-reacted allyl bromide was evaporated under vacuo, diluted with isobutyl alcohol, washed with water (x3), brine, and the solvent evaporated to give a yellow-brown liquid. FTIR was used to confirm the product as allyl polyethylene glycol methyl ether.

The allyl ether (2.2g) in a mixture of triethoxysilane (0.98g, 6.0mmol), H_2PtCl_6 (0.3ml) and THF (10ml) was refluxed overnight under nitrogen to give triethoxysilane-polyethylene glycol methyl ether polymer, which was confirmed by ^1H nmr.

TESTING OF COATINGS

Corks were deliberately spiked with TCA and coated with the coating as described in the procedure below. Tests were then performed to see if the TCA will penetrate through the new coating.

Procedure

The cork was immersed in a solution of 0.1M TCA in absolute alcohol for 24 hours after which it was removed from the solution and dried in an oven at 40°C for another 24 hours. The cork may then be rinsed with a solvent that can dissolve TCA and other off flavoured compounds, eg absolute ethanol or xylene, to remove any excess TCA that may have crystallised on the surface. The cork is then dried in the oven again at 40°C for 24 hours. The cork is now ready for coating.

EXAMPLE 1: COATING SAMPLE PREPARATION FOR AMINOFUNCTIONALISED SILANE POLYMERS

(a) Bistriethoxysilane – BTSE

A solution of varying concentrations of BTSE (20%, 10%, 5%, 2%) in acetic acid and water was stirred for five minutes. Ethanol was added until the solution became clear and then allowed to hydrolyse (48 hours).

Corks were dipped into each solution as described in the method below (section entitled "Dip Coating") and then cured in an oven at 80°C for 10 minutes.

(b) Bistrimethoxysilypropylamine – A1170 (Witco)

A mixture of A1170 (20%, 10%, 5%, 2%) in ethanol was stirred while water (adjust to pH 10 using sodium hydroxide) was added. The corks were immediately dipped into the solution as described below (section entitled "Dip Coating") before the solution solidified into white solids.

The corks were cured in an oven at 80°C for 5-10 minutes.

EXAMPLE 2: TWO DIP PROCESS

Preparation of 2% γ-Aminopropyltriethoxysilane – A1100 (Witco)

A solution of A1100 (2ml) in water (98ml) was stirred and allowed to hydrolyse for 48 hours.

The cork was dipped in 5% BTSE solution (see Example 1(a)), quickly dried using compressed air, dipped in 2% A1100 solution and cured in an oven at 80°C for 10 minutes.

EXAMPLES OF PRE-PREPARED BARRIER FILMS

The multi-layer laminate films that were used were:

PE/MET PET/PE (polyethylene/metallised polyethylene terephthalate/polyethylene)

PE/EVOH/PE (polyethylene/polyethylene vinyl alcohol/polyethylene)

PE/Nylon/PE (polyethylene/nylon/polyethylene)

The film was wrapped to form 1-2 layers around the cork, and was then heated and shrunk to form a continuous envelope around the cork.

EXAMPLE 3: SAMPLE PREPARATION OF THE POLYETHYLENE VINYL ALCOHOL (EVOH) FILMS

Preparation of EVOH-OC(O)NH$(CH_2)_3$ Si$(OEt)_3$

EVOH film (9g) was placed into a reaction vessel and purged with nitrogen for several minutes. Toluene (280ml), isocyanatopropyltriethoxysilane (10ml) and dibutyltin dilaurate (1ml) were added and the reaction was allowed to proceed under nitrogen at 50°C for 24 hours. The film samples was then washed with THF (3x15ml), tert-butyl alcohol (2x15ml), toluene (2x15ml) and dried under vacuum (10 hours). The film was applied to the cork using a heat gun.

Partial co-hydrolysis and condensation of tetramethoxysilane (TMOS) and EVOH-$OCONH(CH_2)_3Si(OEt)_3$

A solution of tetramethoxysilane (101ml) in tert-butyl alcohol (86.6ml), water (12.2ml) and hydrochloric acid (0.2ml) was added to the EVOH-$OCONH(CH_2)_3Si(OEt)_3$ film in a reaction flask. The reaction was allowed to proceed for 48 hours at room temperature, washed with tert-butyl alcohol (3x5ml), water (3x5ml) and toluene (3x15ml) and dried under vacuum for 6 hours.

METHODS OF APPLICATION

Dip Coating

The simplest application method is dip coating, involving a container filled with the coating formulation into which the substrate (such as a cork) is immersed and then withdrawn.

A typical dip coating unit consists of a bath, filled with the coating formulation, and a mechanism on which the substrate is mounted for immersion and withdrawal. It is often necessary to circulate and filter the coating to maintain a homogeneous mixture. A fixing mechanism must be designed to ensure the proper orientation of the substrate during immersion into and withdrawal from the fluid.

Spray Coating

In contrast to dip coating, spray coating operations are much less efficient and much more complicated, as well as being relatively more expensive. Precise control over the spray area is difficult so that masking of the substrate may be required. The advantages

offered by these systems (eg fast application time, very uniform coating thicknesses, and the ability to apply uniform coatings to irregularly shaped objects) may, however, outweigh the drawbacks.

In a spray coating operation, the fluid is atomised into fine droplets for application to the substrate. The size of the droplets formed during atomisation can be controlled by such properties as fluid flow, fluid pressure, air pressure, solution viscosity, and surface tension. A number of different nozzle designs are used in industry, such as compressed air spray nozzles, airless spray nozzles, and hot spray systems.

Slot and Curtain Coating

Slot coating and curtain coating are more appropriate techniques for a continuous operation. The methods involve a stationary die, which delivers a layer of coating onto a substrate moving beneath it. The difference between the methods is in the way that the coating is transferred from the die to the moving substrate. The coating is spread by the slot method when the die slot is close to the substrate; but changing the orientation of the die slot relative to the conveyor and allowing the formulation to cascade is referred to as curtain coating.

Multiple slots in the die face or converging feed to a single slot can produce multilayer coatings.

Roll Coating

Roll coating is another method used in continuous manufacturing operations primarily for coating films. A substrate is fed between two rotating cylinders, while simultaneously directing the coating into the space between the cylinders. Formulation viscosity, speed of the substrate, coating flow rate, and distance between the rolls all contribute to coating thickness and uniformity. Although these systems are limited in the types of substrate that can be coated, they can rapidly produce a very uniform product.

METHODS OF CURING

Thermal Cure

One of the most common methods for initiating the cross-linking of a polymer is by heating, and ovens can be incorporated into batch and continuous-mode systems. The main disadvantage in thermal curing is the wasted thermal energy when only a small amount of the applied energy is transferred to the molecules. It can also be difficult to maintain a uniform temperature throughout the oven, so that curing may be uneven.

Ultraviolet (UV) Cure

One of the most popular techniques used to initiate cross-linking is irradiation by ultraviolet light. It can be a more rapid process than thermal curing, sometimes taking less than a second to act. Very little heat is generated during the exposure, which can often be carried out at room temperature.

Electron Beam Cure

Electron beam (e-beam) radiation shares the same benefits as UV radiation, without the need for a photoinitiation. The exposure forms free radicals that cause the chain reaction.

Gamma-Radiation Cure

Yet another type of irradiation that is rapid at ambient temperatures is γ-radiation cure. Cycle times for γ-ray systems can be longer than for e-beam, at least for conventional polymer matrices, but for curing hydrophilic coatings this does not present a problem.

ADDITIONAL TECHNOLOGIES

Plasma Polymerisation

Thin polymer films can be deposited onto various substrates through the use of plasma polymerisation. A plasma is generated by means of electron excitation, with a gas mixture and an organic monomer. These thin films can be between a few hundred angstroms to a micrometre in thickness. Cross-linking density is usually greater than in conventionally applied coatings, and thin films exhibiting good adhesion can be laid down on virtually any type of substrate.

Surface Grafting

Surface grafting techniques incorporate some of the same general concepts as coating and curing operations but may be more appropriate where exceptionally thin surface layers are desired. Points that distinguish surface grafting from "wet" coating operations are related mainly to the formation of the modified surface layer and the

general molecular structures that result. In conventional coatings, a continuous phase is formed by the reactions of the monomeric or polymeric ingredients, and is adhered to the substrate surface through secondary molecular interactions such as hydrogen bonding, london dispersive forces or acid-base interactions. Primary covalent bonding is also possible if the substrate has been pre-treated with molecular groups. In surface grafting however, the monomeric (or polymeric with reactive end groups) components react directly with a polymeric substrate. Various forms of radiation, such as UV, electron beam, and γ-rays, are used to cause the formation of peroxide groups on the polymer surface. These are unstable so decompose, and cause initiation of polymerisation in the process.

While the present invention has been described in terms of preferred embodiments in order to facilitate better understanding of the invention, it should be appreciated that various modifications can be made without departing from the principles of the invention. Therefore, the invention should be understood to include all such modifications within its scope.

Dated this 22nd day of April 1999.

VINPAC INTERNATIONAL PTY LTD
By its Patent Attorneys
MADDERNS